

PATENT SPECIFICATION

(11) 1389 237

1389 237

- (21) Application No. 32336/72 (22) Filed 11 July 1972
 (44) Complete Specification published 3 April 1975
 (51) INT CL³ B01J 31/18 C07C 3/18 3/56 5/28//C01B 29/00
 (52) Index at acceptance

B1E 282 288 298 300 381 38Y 480 48Y 490 49Y 579 650
 652 678 691 692 693 730 73Y

C1A 6 D16 G30 G30D16

C5E 7A1 7A2 7AY 7B1A2 7B1Y 8A1A2A 8A1B1A 8A1B2
 8A1Y 8A7A1 8A7B1 8A7Y 8A8A1C 8A8Y

(72) Inventor HERMAN SAMUEL BLOCH



(54) HYDROCARBON CONVERSION PROCESS AND CATALYTIC COMPOSITE THEREFOR

(71) We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a novel catalytic composite for hydrocarbon conversion processes which exhibits exceptional catalytic activity in a selective manner. In particular, this invention relates to a novel catalytic composite particularly suitable for use in hydrocarbon isomerization, alkylation and polymerization processes.

In any given hydrocarbon conversion process, the performance of a given catalyst is usually measured by its activity and selectivity. As referred to herein, activity refers to the ability of a given catalyst to catalyze or promote the particular reaction desired in the process at a specified set of reaction conditions, a more active catalyst requiring lower temperatures and lower reaction times (higher space velocities) than those required by a less active catalyst to achieve the same conversion of the reactants. Selectivity refers to the percentage of the converted reactants which have been converted to the desired product(s). A high selectivity is indicative of more complete utilization of the reactants and an absence of undesired side reactions. Thus the art continually strives to develop more active and selective catalysts because of the direct correlation between these parameters and the operating costs of the particular commercial process in which the catalyst is employed.

A further significant property of a catalyst in the determination of its suitability in a given process is its physical form. In general, catalytic reactions are more easily effected when the catalyst exists in particulate form (e.g. spheres or granules of 1/32"—1/2"

diameter) and is contained in a fixed-bed. The reaction may then be conducted by simply passing the reactants over the catalyst. This is contrasted to moving bed operations, wherein the catalyst is constantly circulating either co-currently or counter-currently to the reactants, and fluidized bed operations wherein a micro-sized catalyst is suspended in a fluidized reacting medium. These operations entail greater costs because of the additional solids handling required. Another method of effecting hydrocarbon conversion reactions, in particular isoparaffin alkylation, is to disperse the reactants in a liquid catalyst such as hydrogen fluoride or sulfuric acid. This mode of operation also requires additional steps of catalyst recovery plus the continuous handling of noxious liquid materials. Accordingly, it is a continued goal in the art to develop active selective catalysts suitable for utilization in hydrocarbon conversion processes in a fixed-bed manner. In the particular case of hydrocarbon alkylation such as the production of high octane motor fuels by isobutane alkylation, fixed-bed operations and catalysts suitable for use therein are continually being sought.

We have now discovered a novel catalytic composite which is capable of catalyzing a hydrocarbon conversion reaction at a reaction temperature and/or reaction time greatly below those presently utilized in the art. Furthermore, this highly active catalytic composite catalyzes such reactions in a selective manner, and at such lower temperatures than those typically utilized in the art, that secondary, side reactions are minimized if not eliminated. This catalytic composite is solid and can be effectively utilized in the form of a fixed-bed in a hydrocarbon alkylation process.

According to the present invention there is provided a catalytic composite comprising a porous inert solid support material selected from activated charcoal, activated carbon and graphite having combined therewith an active catalytic complex prepared from antimony

[Price 33p]

pentafluoride and an acid component selected from hydrogen fluoride and fluosulfonic acid.

The catalytic composite may contain from 0.05 to 0.5 parts by weight of acid catalytic complex per part by weight of said support material and the mole ratio of antimony pentafluoride to the said acid component may be from 0.1:1 to 1:1.

The present invention also provides a hydrocarbon conversion process, which process comprises contacting a hydrocarbon, at hydrocarbon conversion conditions, with a catalytic composite according to the invention.

The hydrocarbon conversion process may be an isomerization process, such as the isomerization of either a C_4 — C_8 paraffin or an isomerizable aromatic hydrocarbon; an alkylation process, such as the alkylation of either an isoparaffin or a monocyclic aromatic hydrocarbon in the presence of an olefin; an olefin polymerization process.

The porous inert support material of the catalytic composite of the present invention, e.g. activated charcoal, is preferably one having a surface area of from 50 to 1000 square meters per gram.

The active catalytic complex with which the porous inert solid support material is combined may be a complex of antimony pentafluoride and fluosulfonic acid, of antimony pentafluoride and hydrogen fluoride, or of antimony pentafluoride, hydrogen fluoride and fluosulfonic acid. Particularly preferred are antimony pentafluoride and fluosulfonic acid complexes.

Antimony pentafluoride (SbF_5), hydrogen fluoride (HF) and fluosulfonic acid (HSO_3F , also known as fluorosulfonic acid or fluorosulfuric acid) are compounds well known to the art but whose combination in the aforesaid manner with the above-mentioned porous inert solid support materials as an effective catalytic composite has been heretofore unrecognized. Since antimony pentafluoride has a normal boiling point (B.P.) of $149.5^\circ C.$ and a melting point (M.P.) of $7^\circ C.$, hydrogen fluoride has a B.P. of $19.4^\circ C.$ and a M.P. of $-83^\circ C.$ and fluosulfonic acid has a B.P. of $165.5^\circ C.$ and a M.P. of $-87.3^\circ C.$, the catalytic complexes formed by mixing antimony pentafluoride with either fluosulfonic acid or hydrofluoric acid are liquid solutions at ambient temperatures and pressures. While not to be limited by the following theory, it is believed that antimony pentafluoride-fluosulfonic acid mixtures result in the formation of a $2HSO_3F \cdot SbF_5$ complex which may be considered in its ionic form to be $H_2SO_3F \cdot SbF_5 \cdot SO_3F$. Likewise, an antimony pentafluoride-hydrogen fluoride mixture may be considered as $2HF \cdot SbF_5$ complex in the form of $H_2F \cdot SbF_5$. Accordingly, it is preferred that the mole ratio of antimony pentafluoride to the acid component be about 0.5:1 but it is within the scope of the present

invention for the said mole ratio to be greater or less than this ratio such a complex may then be combined with the foregoing porous inert solid support material to provide a final composite containing from 0.05 to 0.5 parts by weight of the complex per part by weight of said support material. Particularly preferred is a catalytic composite containing from 0.1 to 0.25 parts by weight of the complex per part by weight of the support material and wherein the complex contains fluosulfuric acid and has antimony pentafluoride to fluosulfonic acid mole ratio of from 0.1:1 to 1:1. Also preferred is a composite containing from 0.1 to 0.25 parts by weight of the complex per part by weight of the support material and wherein the complex contains hydrogen fluoride and has an antimony pentafluoride to hydrogen fluoride mole ratio of from 0.2:1 to 0.5:1. Because of their lower volatility and relatively higher acidity, complexes which contain fluosulfonic acid are preferred. However, any reference herein to the term antimony pentafluoride-acid component complex includes within its scope complexes wherein the acid component is hydrogen fluoride in place of fluosulfonic acid. Whichever acid is used, it is essential that the composite be kept and utilized at essentially anhydrous conditions to avoid any decomposition or deactivation of the catalytic complex.

The active catalytic complex may be combined with the porous inert solid support material, such as activated charcoal, by methods known to the art, such as pilling or impregnation, in any form such as spheres, pills or extrudates. Thus the liquid complex may be mixed with activated charcoal in fine particulate form and compressed to form a solid porous catalytic composite containing the desired amount of complex. Since the complex is liquid, another method of manufacture comprises immersing the charcoal in the liquid complex with the sorption thereon of the desired amount of complex. It appears that the complex, although normally liquid, is tenaciously held, because of the physical properties of the mixture, to the carbon by Van der Waals forces or adsorption which permit the catalytic complex to remain relatively firmly combined with the solid inert porous support material even when the catalytic composite is utilized in a hydrocarbon conversion process.

The resulting composite is effective for catalyzing a myriad of hydrocarbon conversion processes such as isomerization, cracking, polymerization, alkylation, disproportionation, transalkylation and dealkylation. Such processes are effected by contacting a reactive hydrocarbon with the afore-described catalytic composite at hydrocarbon conversion conditions in a hydrocarbon conversion zone. This contacting may be accomplished by using the

5 catalytic composite in a fixed bed system, a
moving bed system, a fluidized bed system
or in a batch type operation; however, in
view of the danger of attrition losses of the
catalytic composite and the aforescribed
well known operational advantages, it is pre-
ferred to use a fixed bed system. In this
system, a hydrocarbon charge stock is
brought, via a suitable heat exchanger, to the
10 desired hydrocarbon conversion zone contain-
ing a fixed bed of the catalytic composite. It
is, of course, understood that the conversion
zone may be one or more separate reactors
with suitable means therebetween to ensure
15 that the desired conversion temperature is
maintained at the entrance to each reactor. It
is also to be noted that the reactants may be
contacted with the catalyst bed in either
upward, downward or radial flow fashion. In
20 addition, it is to be noted that the reactants
may be in a liquid phase, a mixed liquid-
vapor phase or a vapor phase when they
contact the catalyst bed, best results being
obtained in the liquid phase.

25 The catalytic composite of this invention
may be used in the isomerization of isomeriz-
able hydrocarbons including paraffins and
naphthenes. It is particularly suitable for use
in the isomerization of straight chain or
30 branched chain paraffins containing four or
more carbon atoms per molecule such as
normal butane, normal pentane, normal
hexane, normal heptane, normal octane and
mixtures thereof. Cycloparaffins applicable
35 are those ordinarily containing at least five
carbon atoms in the ring such as alkylcyclo-
pentanes and cyclohexanes, including
methylcyclopentane, dimethylcyclopentane,
cyclohexane and dimethylcyclohexane. This
40 process also is applicable to the isomeriza-
tion of mixtures of paraffins and/or naph-
thenes such as those derived by selective
fraction and distillation of straight-run
natural gasolines and naphthas. Such mixtures
45 of paraffins and/or naphthenes include the
so-called pentane fractions, hexane fractions
and mixtures thereof. It is not intended, how-
ever, to limit the scope of this invention to
the isomerization of the enumerated saturated
50 hydrocarbons, and it is contemplated that
straight or branched chain saturated hydro-
carbons containing up to 25 carbon atoms per
molecule, including those paraffins contained
in jet fuels and lubes, may be isomerized
55 according to the process of the present in-
vention, C_4-C_{25} paraffinic hydrocarbons
being particularly preferred.

60 The catalytic composite of the present in-
vention also may be used in the isomeriza-
tion of olefins such as a mixture of olefinic
hydrocarbons of approximately the same
molecular weight, including the 1-isomer, 2-
isomer and other position isomers capable
65 of undergoing isomerization to an olefin in
which the double bond occupies a more

centrally located position in the hydrocarbon
chain. The catalytic composite of this inven-
tion can thus be used to provide an olefinic
feedstock for motor fuel alkylation purposes
containing an optimum amount of the more
centrally located double bond isomers by
70 converting the 1-isomer or other near terminal
position isomers into olefins wherein the
double bond is more centrally located in the
carbon atom chain. The catalytic composite
75 of this invention is thus applicable to the
isomerization of isomerizable olefinic hydro-
carbons such as the isomerization of 1-butene
to 2-butene or the isomerization of 3-methyl-
1-butene to 2-methyl-2-butene. Also, the
80 catalytic composite of this invention can be
utilized to shift the double bond of an olefinic
hydrocarbon such as 1-pentene, 1-hexene,
2-hexene or 4-methyl-1-pentene to a more
centrally located position so that 2-pentene,
85 2-hexene, 3-hexene or 4-methyl-2-pentene,
respectively, can be obtained. It is not in-
tended, however, to limit the scope of this
invention to these enumerated olefinic hydro-
carbons as it is contemplated that shifting
90 of the double bond to a more centrally located
position may be effected in respect of straight
or branched chain olefinic hydrocarbons con-
taining up to 20 carbon atoms per molecule.
It is also not intended to limit the scope of
95 this invention to isomerization processes
wherein only the olefinic bond is isomerized
to a new position but also to include within
such scope isomerization processes wherein
the skeletal arrangement of the hydrocarbon
100 is also changed such as the isomerization of
1-pentene to 3-methyl-1-butene and/or 2-
methyl-2-butene. Particularly preferred
isomerizable olefins are the C_4-C_{10} olefins.
Considerable polymerization may accompany
105 olefin isomerization with the use of these
catalytic composites, however, unless extremely
short contact times are used.

The catalytic composite of this invention
also may be used in the isomerization of
110 isomerizable aromatic hydrocarbons including
ortho-xylene, meta-xylene, para-xylene, ethyl-
benzene, the ethyltoluenes, the trimethylben-
zenes, the diethylbenzenes, the triethylben-
zenes, normal propylbenzene, isopropylben-
115 zene and mixtures thereof. Preferred isomeriz-
able alkylaromatic hydrocarbons are the
monocyclic alkylaromatic hydrocarbons, that is,
the alkylbenzenes, particularly the C_6 alkyl-
benzenes and non-equilibrium mixtures of the
various C_6 alkylbenzene isomers. Higher mole-
120 cular weight alkylaromatic hydrocarbons such
as the alkyl-naphthalenes, the alkyl-thracenes
and the alkylphenanthrenes are also suitable.

125 The process for isomerizing isomerizable
hydrocarbons is preferably effected in a con-
tinuous, down-flow, fixed bed system. One
particular method comprises continuously
passing the hydrocarbon to an isomerization
130 reaction zone containing the catalytic com-

posite whilst maintaining the zone at proper isomerization conditions such as a temperature of from $-80^{\circ}\text{C}.$ to $200^{\circ}\text{C}.$, preferably from $-20^{\circ}\text{C}.$ to $100^{\circ}\text{C}.$, and a pressure of from atmospheric to 100 atmospheres. The hydrocarbon preferably is passed over the catalytic composite at a liquid hourly space velocity (defined as volume of liquid hydrocarbon passed per hour per volume of catalyst, hr^{-1}) of from 0.5 to 50. In addition, a diluent such as argon, nitrogen or hydrogen may be present. The reaction product is continuously withdrawn, separated from the reactor effluent and recovered by conventional means, preferably fractional distillation, while the unreacted starting material may be recycled to form a portion of the feed stock.

The catalytic composite of the present invention is also suitable for use in catalyzing hydrocarbon polymerization processes. Such a process may be effected by contacting a polymerizable hydrocarbon with said catalytic composite in the manner described immediately above at a temperature of from $-100^{\circ}\text{C}.$ to $100^{\circ}\text{C}.$, a pressure of from atmospheric to 200 atmospheres and a liquid hourly space velocity of from 0.1 to 10. Such processes may also be effected in the presence of a diluent such as a paraffin, e.g. pentane or hexane, or an aromatic hydrocarbon. Polymerizable olefins suitable for polymerization according to the process of the present invention include the C_2 — C_{10} monoolefins irrespective of the position of the double bond and the molecular arrangement of the carbon skeleton. Thus, 1-olefins such as ethylene, propylene, 1-butene, 1-pentene and 2-methyl-1-butene are as applicable as isobutylene, 2-butene and 2-pentene. Di- and poly-olefins, whether in the conjugated form or not, such as 1,2-butadiene, 1,3-butadiene, isoprene and 1,4-pentadiene, cyclic olefins such as cyclohexene, and alkenyl aromatic compounds such as styrene, alpha-methylstyrene and other alkyl substituted styrenes may be polymerized according to the process of the present invention. The process is applicable to the formation of homo-polymers and co-polymers and to the production of oligomers such as dimers and trimers as well as to the production of higher molecular weight species. Particularly preferred is the polymerization of C_2 — C_6 olefins into a liquid olefin product of higher molecular weight.

The catalytic composite of the present invention is particularly effective for use in the alkylation of an alkylatable hydrocarbon with an alkylating agent. Such an alkylation process is preferably effected by contacting an alkylatable hydrocarbon with the catalytic composite and with an alkylating agent at alkylation conditions including a temperature of from $-50^{\circ}\text{C}.$ to $75^{\circ}\text{C}.$ To prevent polymerization of the alkylating agent, it is preferred that the mole ratio of alkylatable hydro-

carbon to alkylating agent be from 1:1 to 10:1 and that these compounds be intimately mixed with each other before contacting the catalytic composite.

Alkylatable hydrocarbons suitable for alkylation according to the process of the present invention include isoparaffins such as isobutane, isopentane and isohexane, monocyclic aromatic hydrocarbons such as benzene, toluene, ortho-xylene, meta-xylene, para-xylene, ethylbenzene and cumene, and polycyclic aromatic hydrocarbons such as diphenyl, diphenylmethane, naphthalene, anthracene, fluorene and stilbene. Preferred species include the isoparaffins such as isobutane and the monocyclic aromatics such as benzene and toluene.

Alkylating agents capable of alkylating the foregoing alkylatable hydrocarbons include mono-olefins, poly-olefins, alkynes, alcohols, ethers, esters, alkylhalides, alkylsulfates, alkylphosphates and carbohydrates. Preferred alkylating agents for the alkylation of C_4 — C_6 isoparaffins so as to produce high octane number motor fuel include the C_3 — C_4 mono-olefins. Preferred alkylating agents for the alkylation of monocyclic aromatic hydrocarbons, such as benzene or toluene include the C_2 — C_3 mono-olefins although it is within the scope of the present invention to alkylate such aromatic hydrocarbons with higher molecular weight C_4 — C_{20} olefins as utilized in the production of detergent alkylate. In any event, any of the foregoing olefins may be diluted with an inert gas such as hydrogen, nitrogen, methane or ethane, as found in typical refinery streams.

The following is a description by way of example of the preparation of catalytic composites according to the present invention and of their utilization in various hydrocarbon conversion processes.

Example 1

An anhydrous solution containing 33 mole % antimony pentafluoride and 67 mole % fluosulfonic acid was prepared. Activated carbon particles having a relatively spherical shape, a diameter of about $1/16''$, a surface area of about 800 square meters per gram and pore diameters in the 20 to 100 Angstrom range were immersed in this solution for about 2 hours at $20^{\circ}\text{C}.$ The excess solution was then removed, leaving sorbed on the activated carbon about 20 weight % of the original SbF_5 — HSO_3F solution.

Example 2

A catalytic composite comprising an antimony pentafluoride-hydrogen fluoride complex was prepared from a solution containing 3 moles of HF per mole of SbF_5 by a procedure similar to that set forth in Example 1.

Example 3

The catalytic composite prepared in Example 1 was placed in a continuous-flow fixed-bed pilot plant of conventional design. A 10:1 (mole) isobutane to *n*-butylene mixture was continuously passed to this reactor at a liquid hourly space velocity (LHSV) of 5 whilst maintaining the reactor at a temperature of 0°C. and a pressure of 300 psig. The resulting reaction product contained trimethylpentanes and dimethylhexanes, indicating that alkylation had taken place. In a similar manner, a 10:1 (mole) benzene to ethylene admixture was converted to form ethylbenzene.

Example 4

The catalytic composite prepared in Example 1 was placed in a continuous-flow fixed-bed pilot plant of conventional design. Normal butane was continuously passed to this reactor at a LHSV of 4 whilst maintaining the reactor at a temperature of 80°C. and a pressure of 500 psig. Analysis of the resulting reaction product indicated that substantial isomerization of the *n*-butane to isobutane had taken place. In a like manner, essentially pure meta-xylene was isomerized at a LHSV of 2 and a temperature of 100°C. to a mixture of xylene isomers.

Example 5

The catalytic composite prepared in Example 1 was in a continuous-flow fixed-bed pilot plant of conventional design. Propylene was continuously passed thereto at a LHSV of 10 whilst maintaining the reactor at an inlet temperature of about 30°C. and a pressure of about 1000 psig. The resulting reaction product contained considerable amounts of C_6 , C_8 , C_{12} and C_{16} olefin products, indicating that propylene oligomerization had taken place.

WHAT WE CLAIM IS:—

1. A catalytic composite comprising a porous inert solid support material selected from activated charcoal, activated carbon and graphite having combined therewith an active catalytic complex prepared from antimony pentafluoride and an acid component selected from hydrogen fluoride and fluosulfonic acid.
2. A composite according to claim 1, wherein said support material is activated charcoal having a surface area of from 50 to 1000 square meters per gram.
3. A composite according to claim 1 or claim 2 containing from 0.05 to 0.5 parts by weight of said catalytic complex per part by weight of said support material and wherein the mole ratio of antimony pentafluoride to the acid component in the catalytic complex is from 0.1:1 to 1:1.

4. A composite according to claim 3, wherein the acid component of the catalytic complex is fluosulfonic acid and the composite contains from 0.1 to 0.25 parts by weight of the complex per part by weight of the support material.

5. A composite according to claim 3, wherein the acid component of the catalytic complex is hydrogen fluoride, the mole ratio of antimony pentafluoride to hydrogen fluoride is from 0.2:1 to 0.5:1 and the composite contains from 0.1 to 0.025 parts by weight of the complex per part by weight of the support material.

6. A composite according to claim 3, wherein the mole ratio of antimony pentafluoride to the acid component is about 0.5:1.

7. A composite according to claim 1 and substantially as hereinbefore described.

8. A composite according to claim 1 and substantially as hereinbefore described in Example 1 or Example 2.

9. A hydrocarbon conversion process, which process comprises contacting a hydrocarbon, at hydrocarbon conversion conditions, with a catalytic composite according to any one of the preceding claims.

10. A process according to claim 9, wherein said hydrocarbon conversion process is an isomerization process, said hydrocarbon is an isomerizable hydrocarbon, and said conversion conditions include a temperature of from -80 to 200°C.

11. A process according to claim 10, wherein said hydrocarbon is a C_4 — C_8 paraffin.

12. A process according to claim 10, wherein said hydrocarbon is an isomerizable monocyclic aromatic hydrocarbon.

13. A process according to claim 9, wherein said hydrocarbon conversion process is an alkylation process and said hydrocarbon is an alkylatable hydrocarbon which is contacted with said catalyst, in the presence of an alkylating agent, at alkylation conditions including a temperature of from -50 to 75°C.

14. A process according to claim 13, wherein said alkylatable hydrocarbon is a C_1 — C_8 isoparaffin and said alkylating agent is a C_3 — C_8 mono-olefin.

15. A process according to claim 13, wherein said alkylatable hydrocarbon is a monocyclic aromatic hydrocarbon and said alkylating agent is a C_2 — C_8 mono-olefin.

16. A process according to claim 15, wherein said aromatic hydrocarbon is benzene or toluene.

17. A process according to claim 9, wherein said hydrocarbon conversion process is a polymerization process, said hydrocarbon is a polymerizable hydrocarbon, and said conversion conditions include a temperature of from -100 to 100°C.

18. A process according to claim 17,

wherein said polymerizable hydrocarbon is a C_2-C_8 olefin.

carbon conversion process as claimed in any of claims 9 to 20.

- 5 19. A hydrocarbon conversion process as claimed in claim 9 and substantially as hereinbefore described.

20. A hydrocarbon conversion process as claimed in claim 9 and substantially as hereinbefore described in any one of Examples 3 to 5.

- 10 21. A hydrocarbon produced by a hydro-

J. Y. & G. W. JOHNSON,
Furnival House,
14—18, High Holborn,
London, WC1V 6DE,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.